DEVELOPMENT OF EQUILIBRIUM MODEL OF VACUUM DISTILLATION FOR BENZENE/TOLUENE SEPARATION USING MOSAIC SOFTWARE

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ABSTRACT

This paper presents development of equilibrium model of vacuum distillation for benzene/toluene separation using MOSAIC software. The vacuum distillation process was modeled using MOSAIC software by key in the relevant equations and functions that related to vacuum distillation. The generated code from MOSAIC then transferred to MATLAB® environment to get the data for plotting the graph of temperature and composition profiles of vacuum distillation. The range of temperature in the vacuum distillation column was from 299 K to 318 K. The separation of benzene and toluene using vacuum distillation produce high purity of benzene at distillate which was 85 % of vapour mole fraction at distillate stream. Meanwhile, 92% of vapour mole fraction at bottom stream was toluene.

ABSTRAK

Tujuan kajian ini dibuat adalah untuk membangunkan model penyulingan vakum dalam keseimbangan bagi pemisahan benzene/toluene dengan menggunakan perisian MOSAIC. Proses penyulingan vakum dimodelkan dengan memasukkan persamaan dan fungsi yang berkaitan penyulingan vakum ke dalam perisian MOSAIC. Kod dihasilkan daripada MOSAIC kemudian dipindahkan ke persekitaran MATLAB® bagi mendapatkan data untuk memplot graf profil suhu dan komposisi penyulingan vakum. Julat suhu dalam ruang penyulingan vakum adalah dari 299 K hingga 318 K. Pemisahan benzena dan toluena menggunakan penyulingan vakum menghasilkan benzena berketulenan tinggi dimana 85 % daripada pecahan mol cecair pada aliran sulingan adalah benzena. Sementara itu, 92 % daripada pecahan mol cecair pada aliran bawah adalah toluena .

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NOMENCLATURE

F	Feed molar flow rate	mol/s
H	Enthalpy	J/mol
L	Liquid molar flow rate	mol/s
M_j	Molar liquid hold up on stage j	mol/s
P	Total pressure	Pa
P^o	Saturated vapour pressure	Pa
t	time	s
T	Temperature	K
V	Vapour molar flow rate	mol/s
x	Liquid composition	-
y	Vapour composition	-
z	Feed composition	-

Greek letters

ϕ	Fugacity coefficient	-
γ	Activity coefficient	-

Subscripts

i	Component number
j	Stage number

Superscripts

c	Total number of components

List of abbreviations

EQ	Equilibrium model
Bz	Benzene
Tol	Toluene
VD	Vacuum distillation

1 INTRODUCTION

1.1 Motivation and statement of problem

Vacuum distillation (VD) is actually an ordinary distillation but operate at lower pressure. The lowered pressure in distillation column reduces the boiling point of the components in the mixture. As the result, VD is commonly used in petrochemical industry to separate high boiling point hydrocarbon mixture. It also used to avoid cracking the long chain hydrocarbon if the mixture is subject to high temperature. Many researchers had produce various research to expand the application of vacuum distillation such as removal of impurities from crude nickel (Liu et al., 2012), removing lead from metallic mixture of waste printed circuit boards (X. Li, Gao, & Ding, 2013) batch operation for sulfuric acid recycling (Jung, Song, Park, Na, & Han, 2014), removal of impurities from crude lead with high impurities (Kong, Yang, Xiong, Liu, & Xu, 2014), separation of Sn-Sb alloy(Wang et al., 2014), recovery of titanium from the slurry formed in crude $TiCl_4$ (Xiang, Wang, Wang, & Chen, 2014), separation of elemental sulfur from zinc concentrate direct leaching residue (H. Li et al., 2014) and preparation of Te nano powder (Kim et al., 2014).Toluene and benzene are important chemicals because these chemical compounds are used as intermediate to produce other chemicals. Benzene for example is used to produce ethylbenzene, cumene and cyclohexane. Meanwhile, most of toluene converted to benzene and used to produce toluene diisocyanate (TDI).

The development and implementation of new models is hard and expensive task. This is because the complexity and low reusability of process models (Mangold, Motz, & Gilles, 2002). Although with existence advanced modeling in market, model formulation and configuration is still time consuming process in process modeling (Lam, Li, & Xu, 2007).

Modeling of vacuum distillation can be done by using available commercial software such as MatLab. This software requires the modeler to have extensive knowledge of process and prone to produce error due to long and complicated codes. Other software like AspenPlus is more to simulation of the chemical process rather than modeling and cannot be used to produce custom models.

The introduction of MOSAIC modeling software had been a great help for the modeler to create mathematical models for chemical processes. The unique feature such as latex enables the user to key in mathematical expression as close as possible to the literatures. Besides that, MOSAIC enables the code generation and translates it into different kinds of program code such as C++.

1.2 Objectives

The following are the objectives of this research:

- To explore the modelling of VD of benzene/toluene separation by using MOSAIC

1.3 Scope of this research

The following are the scope of this research:

i) Modelling of equilibrium(EQ) model of VD by using MOSAIC based on the given parameters of benzene/toluene separation

ii) Validation of the modelled VD with results from Aspen Plus

iii) Comparison between MOSAIC and other modelling environments.

2 LITERATURE REVIEW

2.1 Vacuum Distillation Column

2.1.1 General Introduction

Vacuum distillation (VD) is one of the separation unit found in refinery plant. The function of VD is to increases the amount of middle distillates and produces lubricating oil base stock and asphalt. VD is used to prevent cracking long chain hydrocarbons present in feed (Matar & Hatch, 2000).

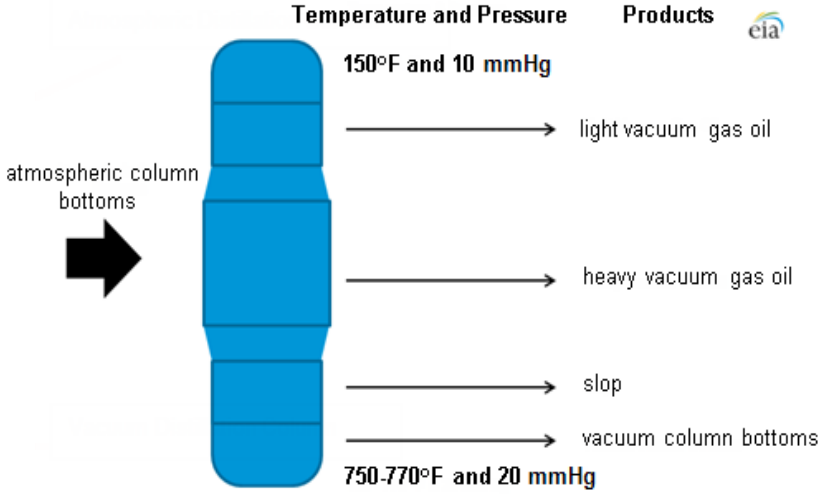

Figure 1: The products from VD in refining plant (U.S. Energy Information Administration, 2012)

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The working principles of VD is the boiling point of mixture will be decrease when the pressure is low. The lower boiling point that can achieve in VD compare to atmospheric distillation had made VD preferable as separation method for heat sensitive material such as foods, fruit juices, drugs and plant extracts.

2.1.2 Advantages of VD

Besides the reduction of boiling point of mixture, VD also increases the relative volatility. In vacuum condition materials are more volatile hence more evaporation takes place. More products will be collected at distillates, hence higher production rate.

By using VD, reduction of energy consumption can be achieved as the result of lower boiling point of mixtures. Atmospheric distillation column tends to use huge amounts of energy because of the evaporation process. According to Kunesh *et. al* (1995), the

reboilers of distillation columns use more than half of the process heat distributed to plant operations. So, VD is good separation alternative to reduce reboiler operating cost in plant.

The vacuum condition effect the position of azeotropic point for azeotropic mixture by shifting up the point. Hence, the separation of azeotropic mixture is easier when the vacuum condition is employed in distillation column (Repke & Klein, 2005).

2.1.3 The drawback of VD

Despite of few advantages of VD, this separation technique has the drawback of requiring large size of condenser. Vacuum condition reduce the vapour dew point, hence the condenser loses the driving force for heat transfer which is mean temperature difference (MTD). More surface area is needed for the condenser to work properly. As the result, the company has to pay high installation cost (Jung et al., 2014)

2.2 Benzene and Toluene

2.2.1 Global market of benzene and toluene

At present, the Asia-Pacific is the largest consumer of benzene and all of its downstream derivatives, which consumed more than 45.0% of the total consumption in 2012. Among all the countries, China dominates the benzene market, which consumed the maximum volume of benzene in 2012. The overall benzene demand is driven by the producers of ethylbenzene, cyclohexane, and cumene which consuming almost 82.0% of the total demand in 2012. Cumene manufacturing segment is expected to be the largest user of benzene which is primarily driven by growing demand for phenol and acetone (PRNewswire, 2014).

Throughout the world, consumption for toluene in virtually every region was negatively impacted by the economic recession in 2008 and/or 2009. The developed regions (North America and Western Europe) declined 8% and 17%, respectively. However, three regions increased their production of toluene over the same time frame—the Middle East, Northeast Asia and Southeast Asia. Since 2010, most regions have experienced growth. The fastest growing regions are Africa, the Indian Subcontinent and Northeast Asia.

However, demand in developing regions such as China, Thailand and the Middle East saw continued growth during this period. As global economies begin to slowly recover, toluene markets are anticipated to improve (IHS Chemical, 2013).

2.2.2 Application of benzene and toluene

Benzene and toluene are manufactured from fractions of crude oil distillation. Half of the benzene manufactured is used to produce ethylbenzene the raw material to make polystyrene. Another quarter is to produce cumene, which is then use to make phenol and acetone. Besides that, benzene is use to make cyclohexane, the important intermediate to make adipic acid and caprolactam. Meanwhile, over 50% of toluene produced is converted into benzene. Toluene is also used to make TDI (toluene diisocyanate), important chemical in production polyurethanes. In addition, toluene also widely used as solvent for alkyd polymers (University of York, 2014)

2.2.3 Benzene and Toluene Synthesis

Nowadays, 80 % of benzene and toluene are primarily produced via:

1. Steam cracking of naphtha
2. Catalytic reforming of naphtha

Small amount of benzene which is about 20 % are produced from toluene using:

1. dealkylation
2. disproportionation (University of York, 2014)

2.3 Equilibrium MODEL of VD

2.3.1 Assumptions of VD Models

There is no available model for benzene/toluene vacuum distillation column but the assumptions made by Kulkarni (1995) for xylene/toluene column can be used as guidance. These assumptions were:

1. Each tray is a sieve tray.
2. Vapour holdup on each tray is negligible.
3. Liquid holdup on each tray varies with time.
4. Due to lower pressure, ideal gas behaviour describes the vapour phase.
5. Raoult's law describes the vapour-liquid equilibrium (VLE) relationship.

6. Sensible heat changes on each tray are negligible.
7. Negligible secondary heating effects due to mixing.
8. Reflux from the accumulator is a saturated liquid.
9. The reboiler is an equilibrium stage,
10. All vapour is condensed in the condenser.

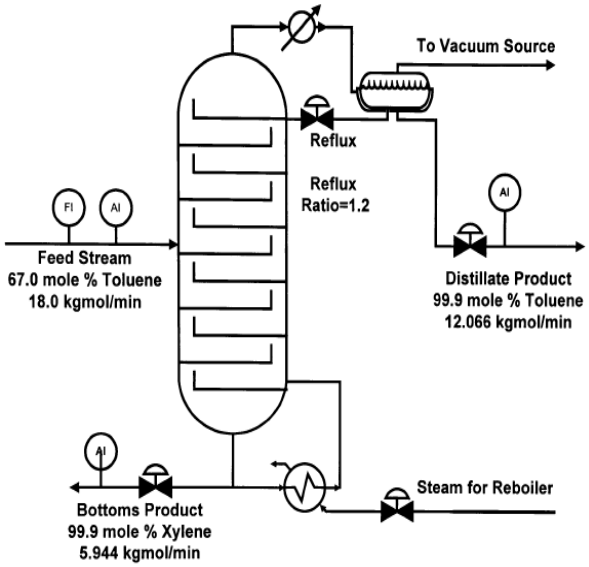

Figure 2: Xylene/Toluene High Purity Distillation Column (Anderson, 1998)

2.3.2 Mathematical Modelling of EQ

The first step of modelling begins with mathematical modelling by formulation of equations to describe processes occurring in RD at the steady state. These formulated equations or just MESH equations will be required in finding solution of the model. The letters of MESH stand for material balance equations, phase equilibrium equations, summation equations and heat balance equations.

Material balance equations

The material balance of every stages of VD can be represented by equation as follow:

Overall material balance

$$\frac{dM_j}{dt} = F_j - L_j - V_j + V_{j+1} + L_{j-1} + \delta_j R_j$$

Components material balance

$$\frac{dM_j x_{j,i}}{dt} = F_j z_{j,i} - L_j x_{j,i} - V_j y_{j,i} + V_{j+1} y_{j+1,i} + L_{j-1} x_{j-1,i} + \delta_j \sum_{r=1}^{R} \left(v_{i,r} r_{j,r} \right)$$

(Murat, Mohamed, & Bhatia, 2003)

Since the model is assumed as steady state, and thus the derivative of material balance will be equal zero. Both j and i are subscripts to represent the stages numbers and components respectively. F represents feed flow rate, L represents liquid flow rate then V will represent vapour flow rate. x and y are the mole fraction of liquid and vapour respectively.

Furthermore, for integrated reactive part of equation, r represents the reaction rate and v represents the stoichiometry of chemical components. The value of δ will be either 0 or 1 to decide whether reaction occurring at the stages or not. As there is no reaction in column, the integrated reactive part and the value of δ are assigned zero.

Phase equilibrium equations

$$y = \frac{\gamma P^o x}{\phi P}$$

Phase equilibrium relation equation describes the relationship between liquid mole fraction and vapour mole fraction of chemical components when vapour and liquid at equilibrium state. For the ideal condition, the value of activity coefficient, γ and fugacity, ϕ will be equal to 1. Saturated vapour pressure, P^o can be calculated using of Antoine equation and P is pressure of reactive distillation column.

Summation equations

$$\sum_{i}^{c} x_{j,i} = 1.0 \qquad \text{(Liquid phase)}$$

$$\sum_{i}^{c} y_{j,i} = 1.0 \qquad \text{(Vapour phase)}$$

From the summation equation, it states that sum of mole fraction of each component in liquid phase and vapour phase of each stage will be equal to 1.

Enthalpy balance equations.

The energy balance of each stages of VD can be described by equation as follow

$$\frac{dH_j}{dt} = F_j H^F + L_{j-1} H^L_{j-1} + V_{j+1} H^V_{j+1} - V_j H^V_j - \delta_j \sum_{r=1}^{R} \left(\Delta H^R_{j,r} \right) r_{j,r}$$

(Murat et al., 2003)

Again, for the steady state, the derivative of energy balance will be equal to zero. The reactive part of the equation, ΔH is enthalpy change of chemical reaction, r is the rate of reaction and δ will decide whether the reaction taking place at each stages or not. The summation of enthalpy change can be ignored as there is no reaction occurs in the column.

2.4 MOSAIC

2.4.1 Introduction

MOSAIC is web-based modelling environment that ease the modelling works by:

1. Minimizing the modelling errors.
2. Minimizing the programming effort.
3. Avoiding the errors in documentation.

Encouraging and supporting the cooperative work.(Kuntsche, Barz, Kraus, Arellano-Garcia, & Wozny, 2011)

2.4.2 Advantages of Using MOSAIC

One of the sources of error in programming of models is the visual difference between mathematical expressions in documentation and the calculation expression in program code. In MOSAIC modelling environment, this type of error is minimized by defining the model equations directly in two-dimensional mathematic expressions. The use of documentary language standard such as Latex is a good way to define model equations in mathematic symbolic language.

MOSAIC software has versatile code generation functionality. The output of MOSAIC is program code that can be use as a solution for simulations problems. The models created using MOSAIC are independent from programming languages thus can be used as input for other modelling tool software.

As the MOSAIC is web based software, model data base can be access over the internet. The data base contain both the model related equations, equation systems and calculation studies and the necessary data like simulation results, measurement data for

model validation, and meta information. These features offer the reusability of the models created by the various developers.

2.5 Summary

The implementation of VD for separation purpose had brought many benefits in chemical, food, pharmaceutical and waste treatment industry. The ability of VD to separate mixture at lower temperature than atmospheric distillation makes it suitable for heat sensitive materials such as plant extract, protein and polymers.

3 METHODOLOGY

3.1 Conditions for Benzene/Toluene VD Column

3.1.1 Assumptions Used In Modelling

The feed that enter the VD column can be assumed to contain only benzene and toluene. In real situation, the feed usually contain other long chain carbon groups and aromatics. As the concentration of these components is low it can be neglect.

3.1.2 Conditions of Benzene/Toluene Separation

The data used for modelling the benzene/toluene VD were taken from xylene/toluene column as it has close chemical and physical properties. The distillate flow rate is 12.066 kmole/min. The feed temperature is 95 °C and entered at tray number 24 from bottom. There are 49 trays with column diameter of 3.962 m (Anderson, 1998).

3.2 Procedure of using MOSAIC

Step 1: Creating of notation

The symbols with description are created in notation to represent the variables of equations. Each variable can be represented by base name alone or together with subscripts and superscripts. A notation can be valid for an entire model or only a small portion of it. By introducing of subscripts and superscripts, it allows two or more variables to have similar base name. Besides the creating of symbols for each variable, the indices required for modelling are created as well in notation.

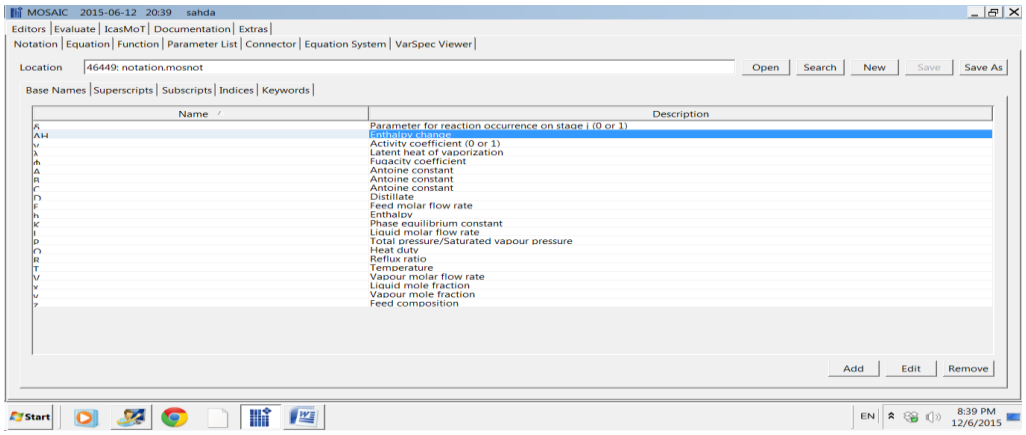

Figure 3: Generating of notation

Step 2: Creating of equation objects

The modelling equations can be created by using of Latex. Latex is a documentary language which allows equations to be expressed in documentation level. Other than basic equation systems, MOSAIC only supports differential algebraic equation systems of first order at the moment (Esche et al., n.d.).

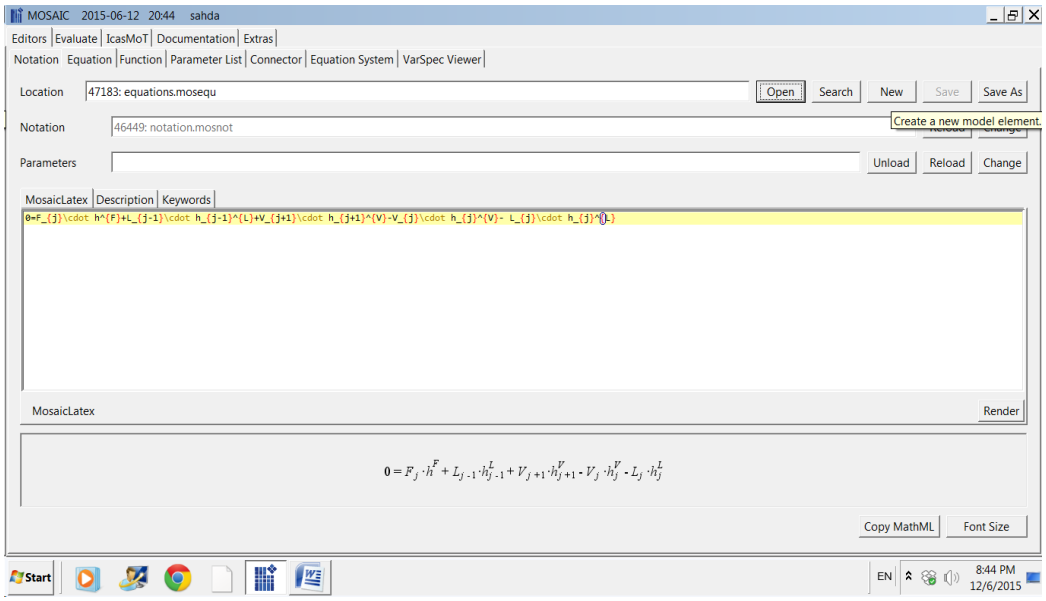

Figure 4: Generating of equation

Step 3: Creating of functions objects

Almost same as creating of equation objects, function objects are created by using Latex as well. However, the method of creating functions is not as simple as creating of equations. It may require creating of parameter list object if involving in parameter set index. Parameter set index allows users to set the index on output variable and parameters. The specification of output variable and input variables will be required. The output variable will be the variable that is calculated while the input variables are almost similar as design variables where the setting of its values will be required. Lastly, the formula which leads to output variable will be written in form of Latex.

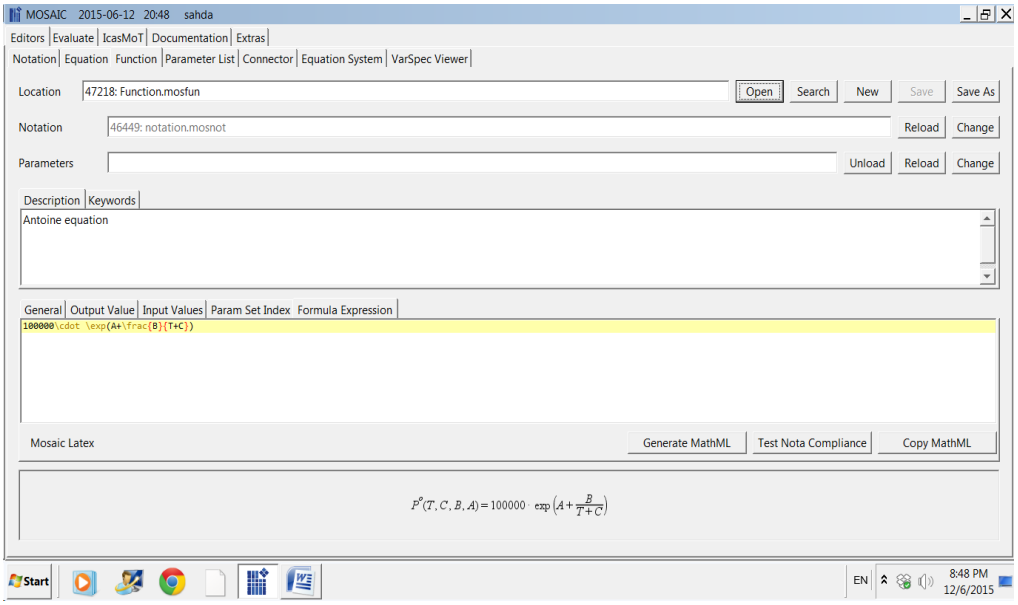

Figure 5: Generating of function

Step 4: Creating of equation system

All equations and functions of a model are connected by equation system for evaluation. Adding of equations to equation system can be done easily, but for adding of functions, it is required to set the output variables and input variables. Preview of all the added equations and functions in equation system can be made.

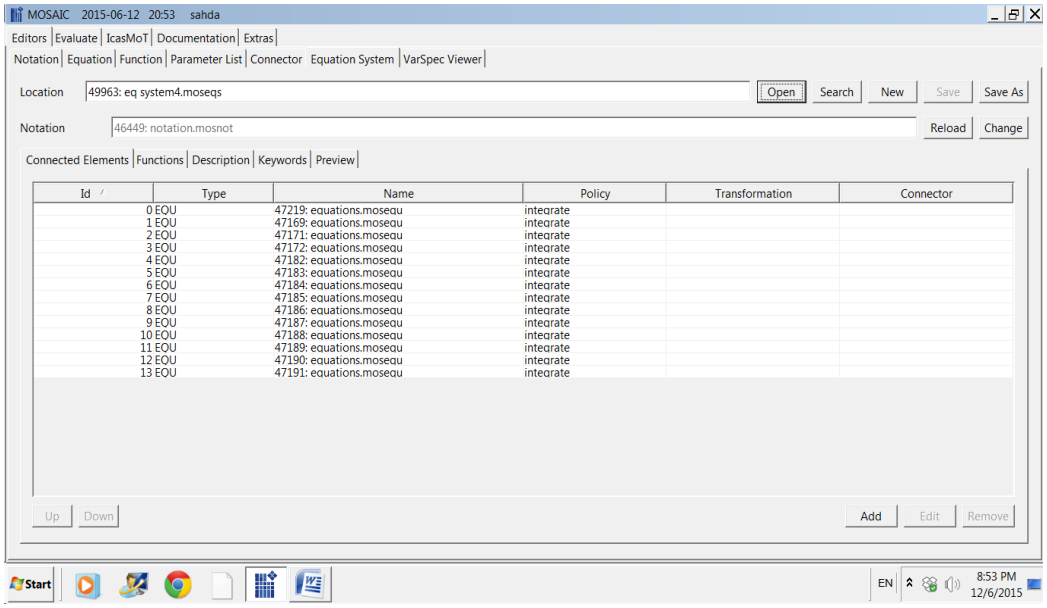

Figure 6: Process of adding modelling equations

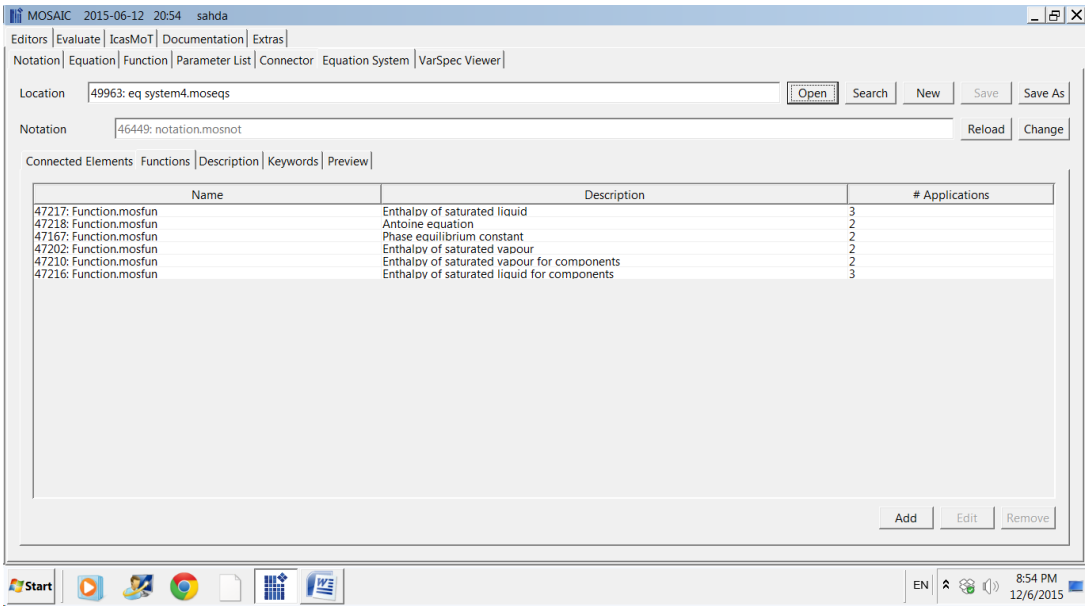

Figure 7: Process of adding modelling functions

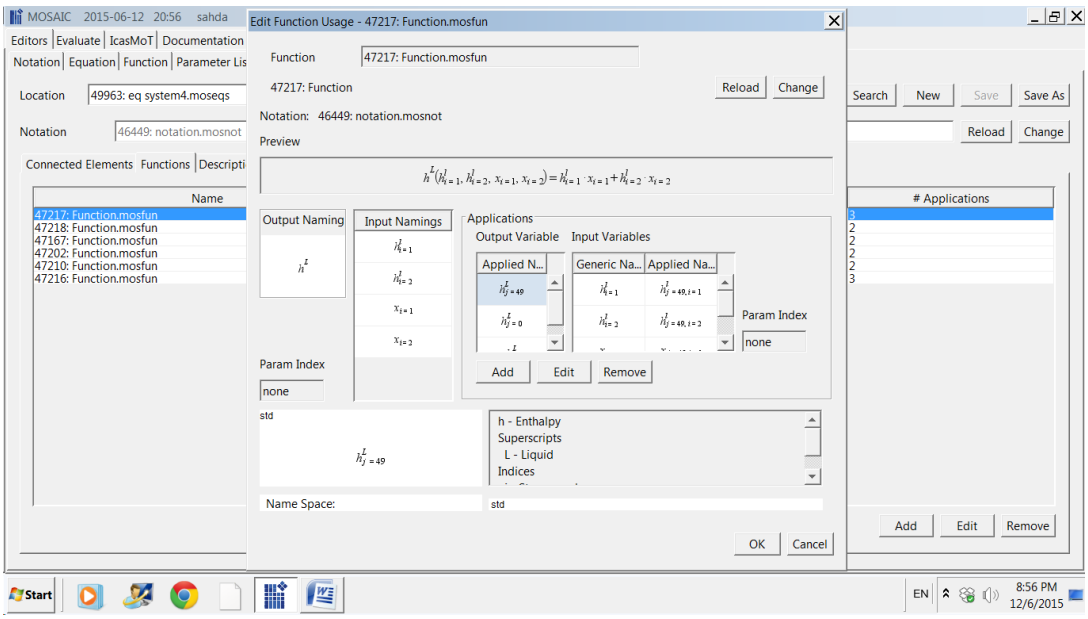

Figure 8: Process of adding the functions of applications

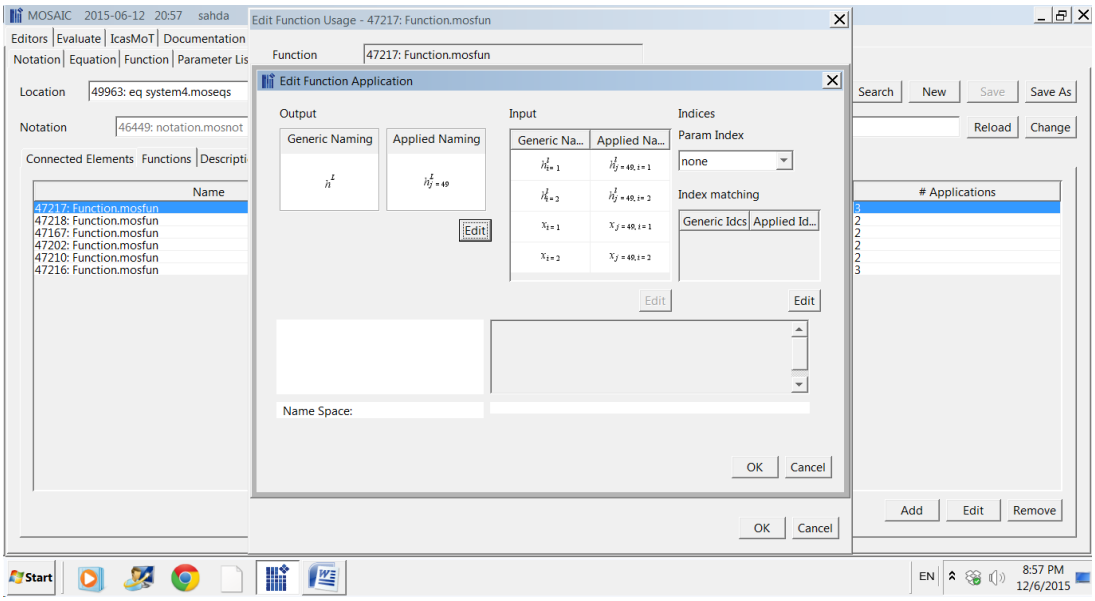

Figure 9: Process of setting the input variables

Step 5: Creating of evaluation object

In order to create the evaluation object, the equation system first has to be loaded. Once it is loaded, indexing can be made by specifying the max value of each index. After indexing, all the equations and functions involved in modelling can be displayed.

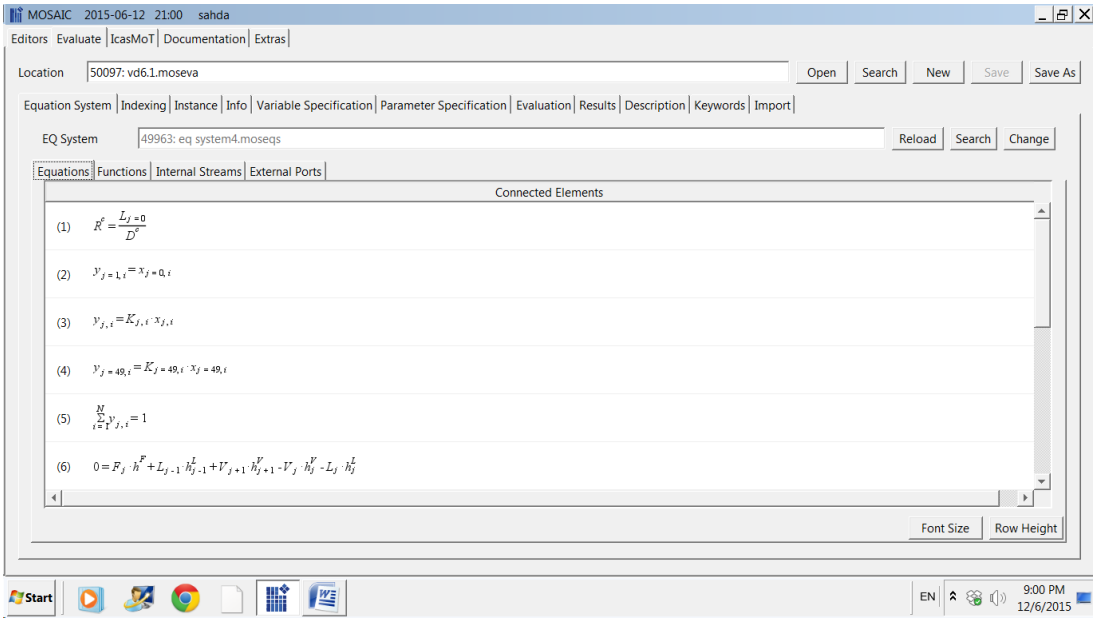

Figure 10: Preview of equation system

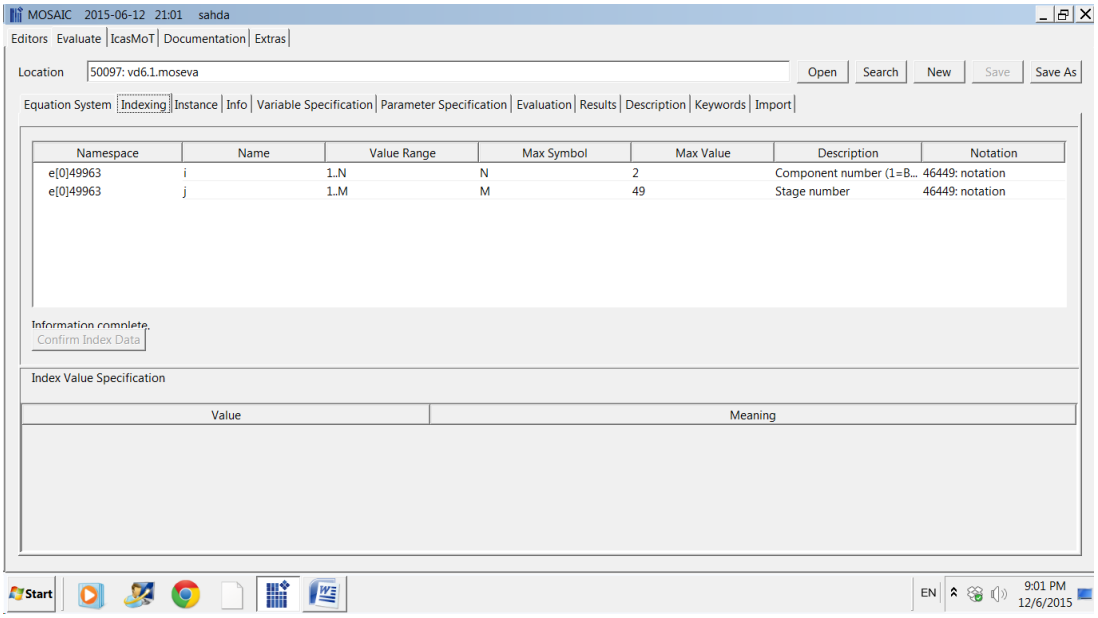

Figure 11: Process of setting the index number

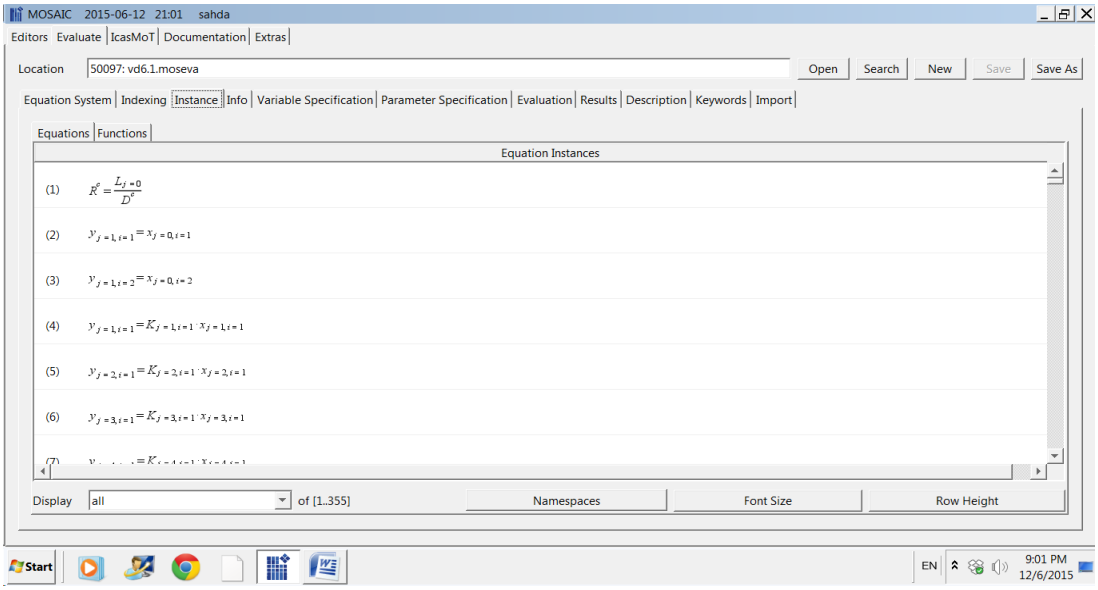

Figure 12: Preview of modelling equations after indexing

Step 6: Creating of parameter object

Specifications of variables are now ready to be made by assigning the variables as iteration variables or design variables. The degree of freedom will be automatically calculated when assigning of variables. In order to solve the model, degree of freedom must be zero. Once it is done, the value of each design variables is given for calculation. Furthermore, good initial values of iteration variables are important in solving of model.

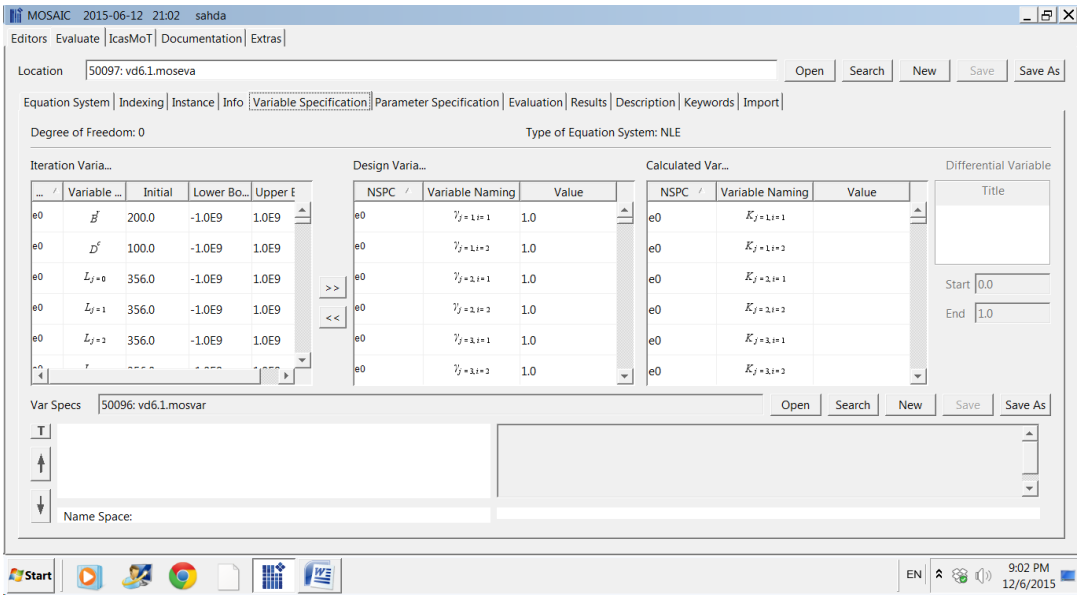

Figure 13: Process of setting variable specification

Step 7: Code generation and evaluation

MOSAIC is not designed to be full solver as it is not able to solve complex models. The solving of model can be made by code generation for other modelling environments. The generated codes can be run at their own environment for the solving of model.

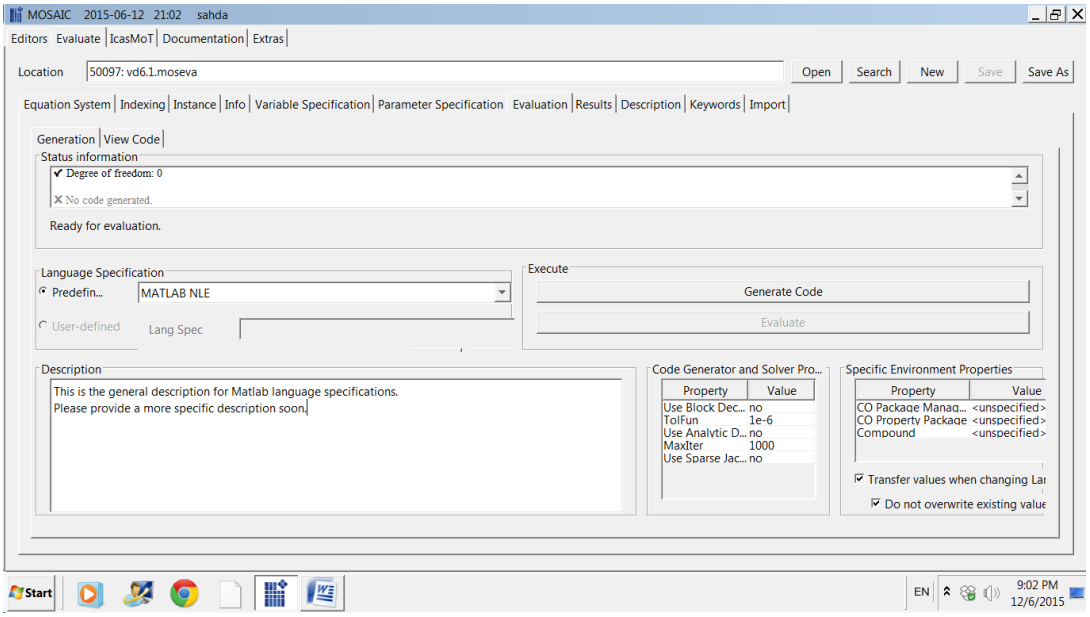

Figure 14: Process of generating code